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n-Hexane isomerization on Ni-Pt catalysts/supported on HUSY zeolite: The influence from a metal content

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Abstract

Bi-functional catalysts were prepared to contain Ni, Pt or both, supported on a HUSY zeolite, with the following metal contents: catalysts 30, 130 and 180 × 10^{-6} atg metal/g catalyst. These catalysts resulted from a competitive ion exchange with the use of aqueous solutions from $[Ni(NH_3)_6]Cl_2$ and $[Pt(NH_3)_4]Cl_2$ complexes. The catalysts were provided with a scheduled temperature reduction (TPR) and subjected to a catalytic assessment on the n-hexane isomerization at 250 °C and 1 atm. TPR results showed larger reducibility of Ni^{+2} cations in the presence of Pt. Bi-metallic Ni-Pt catalysts showed to have smaller deactivation and much higher activity compared to monometallic Ni catalysts. The selectivity for the production of di-ramified alkanes increases as the Ni content increases.

Keywords: n-Hexane; Isomerization; Octane; Bi-metallic catalyst; Ni-Pt

1. Introduction

In the last few decades, the introduction of environmental policies has restricted the use of some components used in fuel composition. This has caused oil refineries to continuously reformulate their gasoline composition in an attempt to keep or improve their product quality while minimizing adverse effects to men and the environment.

These concerns have led to the implementation of regulations limiting the addition of aromatic compounds (particularly benzene) and tetraethyl lead to gasoline. Removing these compounds has had a negative impact on gasoline octane content and many studies have been developed designed to increase gasoline octane content by other means [1,2].

Gasoline containing high quantity of linear-chain compounds has low octane content. However, such content can be increased when gasoline is subjected to an isomerization process through which linear-chain molecules are converted into ramified molecules [3]. In an attempt to make this process viable to the industry, an isomerization process can be performed on solid catalysts containing metallic sites and acidic sites (bi-functional catalysts) [4]. These are catalysts containing metals supported on silica or alumina. However, it has been reported that replacing these supports by zeolites can provide significant advantages to catalysts, such as additional activity and selectivity.

In the industry, catalysts that are most frequently used for isomerization of linear-chain alkanes usually contain Pt, which is supported on chlorinated alumina. However, this process requires a continuous addition of small amounts of chlorinated organic compounds, which can lead to corrosion issues [5]. For this reason, various studies have been developed to replace amorphous supports with zeolites, which have acid sites density 10–1000 times higher than amorphous alumina or silica–alumina supports. Additionally, zeolite-supported catalysts have expressive activity increases for the formation of ramified-chain molecules.

One of the advantages of zeolites over other kinds of catalysts is related to their crystalline microporous structure. Zeolites structural properties can offer many possibilities to a large number of chemical reactions [6]. Current researches

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have been focused on the development of zeolite-supported catalysts to be used in oil refining processes [7].

The Y/Ni/Pt zeolite combination has proven to be one of the most significant and attractive routes for the isomerization of linear-chain alkanes. In addition to the vast amount of information available in the literature related to this catalyst, monofunctional Pt catalysts are being replaced with other catalysts that can perform the same function without the same disadvantages. Bi-functional catalysts can meet these expectations, in an attempt to replace those that are associated with high costs with ones that are more cost effective and provide additional selectivity and conversion to targeted products.

According to results achieved in this laboratory, adding a second metal to the zeolite structure (forming a bi-metallic catalyst) can cause a significant increase to catalyst activity and selectivity and to the formation of ramified compounds. To identify changes from the addition of a second metal, characterization techniques have been used to establish a direct or indirect relationship between the changes in the properties and the catalytic performance.

Because cation reducibility in the zeolite fundamentally depends on its reduction potential and its interaction with the zeolite [8], it is possible, from TPR profiles, interfere on the different degrees of metallic ion reduction and their location in the zeolite cavities. For Ni-Pt catalysts-supported Y zeolite, it has been reported that ions, which are located in large cavities are more easily reduced than those present in small cavities [9]. Additionally, Ni is more easily reduced in the presence of Pt, which is evidenced by the shifting of reduction peaks to lower temperatures.

Most studies using bi-metallic catalysts are performed with catalysts having a constant mass, which can lead to wrong readings. This is due to the fact that, in the case of Pt-Ni, the atomic masses of both metals are different (195.09 versus 58.71, respectively). In this light, the objective of this paper is to report the influence of Pt on the reduction and on the properties of Ni^{+2} catalysts that are supported on zeolite HY. In this study, catalysts containing a constant metal content will be compared.

2. Experimental

2.1. Preparation of Ni and Pt/HUSY monometallic catalysts

The ultra-stabilized commercial zeolite Y (HUSY, Si/Al ratio = 11) was supplied by Engelhard and used as the starting material, as in previous studies [9]. The zeolite was subjected to a competitive ion exchange [12] at room temperature through a solution containing NH_4^+, to change its protonic form (HUSY) to the ammoniacal form (NH_4USY). The ion exchange made possible increased efficiency of the ion exchange using metal cations, which would be performed later.

The Nickel-containing catalysts were obtained by subjecting NH_4USY zeolite to a competitive ion exchange involving the cations of the metal complex $[Ni(NH_3)_6]^{2+}$ and NH_4^+ ions. For this, a solution of 0.05 mol L^{-1} $[Ni(NH_3)_6]Cl_2$ containing NH_4^+ (to give an $NH_4^+/[Ni(NH_3)_6]^{2+}$ ratio of 20) was used. To perform the exchange, the solution was added slowly (0.2 mL min^{-1}, while stirring at room temperature) to a suspension of NH_4USY that contained the volume of water required to give a final concentration of 0.005 mol L^{-1} $[Ni(NH_3)_6]^{2+}$. After a period of 70 h, the solid was separated by filtration, washed with deionized water and dried at 110 °C for 2 h. The solution that separated during filtration was analyzed for metals with atomic adsorption spectroscopy (AAS) in order to determine the real metal content in the solid.

For the precursors containing only Pt-supported on NH_4USY, the same methodology as described for Ni was used, with the exception that $[Pt(NH_3)_4]^{2+}$ (instead of $[Ni(NH_3)_6]^{2+}$) was used at a molar ratio of 10.

2.2. Preparation of bi-metallic Ni-Pt/HUSY catalysts

To obtain the precursors of the Ni-Pt bi-metallic catalysts, two solutions that were identical to those described above were prepared. One solution contained $[Ni(NH_3)_6]Cl_2$ and the other $[Pt(NH_3)_4]Cl_2$. These solutions were added simultaneously to the NH_4USY zeolite suspension—following the same procedure described for the mono-metallic catalysts. After stirring for 70 h, the solid was separated by filtration, washed in deionized water and dried at 110 °C for 2 h.

2.3. Calcination

After the precursors were prepared, they were submitted to calcinations. This was done to remove the ligands co-coordinated to the metal and decompose the NH_4^+ cations that are present in the NH_4USY zeolite, thus, forming Brönsted acid sites (HUSY). The samples were heated at 10 °C min^{-1} rate from room temperature to 100 °C, under a flow of N_2 (100 cm^3 min^{-1} g_{cat}^{-1}) and the sample remained at this temperature for 1 h. Then, the samples were subjected to a compressed air flow (100 cm^3 min^{-1} g_{cat}^{-1}) and the temperature was increased up to 500 °C at 2 °C min^{-1}. With the samples remaining under the air flow, the 500 °C temperature was kept constant for 2 h, in order complete the calcination process.

2.4. Temperature programmed reduction

Calcinated samples were characterized by TPR (Micromeritics-ChemiSorb 2705), under a mixed flow of H_2–N_2 (5% H_2 30 mL min^{-1}). Approximately, 150 mg of the sample were heated at a rate of 10 °C min^{-1} in the range of 20–1000 °C. Before beginning data acquisition, the samples were subjected to a pre-treatment process that consisted of heating from room temperature up to 200 °C (at 10 °C min^{-1}) and keeping this temperature for 1 h under a N_2 flow (30 mL min^{-1}).

2.5. Chemisorption and catalytic evaluation

Before catalytic testing, catalysts were dried at 200 °C, under a N_2 flow (32 mL min^{-1}), for 60 min and then subjected to in situ reduction under a flow of H_2 (55 mL min^{-1}). For this reduction, catalysts were heated from room temperature up to approximately 500 °C (at 2 °C min^{-1}). The catalysts remained at this temperature for 6 h to ensure that the reduction of the metal ions was complete.

For chemisorption, after reduction, the catalyst was cooled to room temperature under vacuum (5×10^{-5} Torr) and the first isotherm was performed at an interval of 0–100 Torr H_2. Then, the samples were placed under vacuum for 2 h and the second isotherm was carried out (0–100 Torr H_2). The quantity (Q_1) of H_2 chemisorbed was calculated by subtracting the 2nd isotherm (chemisorption) from the 1st (chemisorption and physisorption).

Catalysts activity and stability were evaluated for reaction times of 6 h during the isomerization of *n*-hexane at 250 °C temperature (1 atm). H_2 and *n*-hexane were fed into the reactor at 55 and 2 mL h^{-1}, respectively, giving a molar ratio of 9:1 (H_2:*n*-hexane). Products present in the gas flowing from the reactor were analyzed by gas chromatography (Varian-model STAR 3400Os).

3. Results and discussion

3.1. Scheduled temperature reduction

Fig. 1 shows TPR profiles of the monometallic catalysts (Ni or Pt/HUSY) and the bi-metallic catalysts (Ni-Pt/HUSY).

Reduction peaks for Ni^{2+} and Pt^{2+} have been attributed [10] to cations situated in different positions in the zeolite Y. When the peak is formed at lower temperatures (α) cations are located in large cavities, while for the ones formed at higher temperatures, the cations are in sodalite (β) or hexagonal prism cavities (γ).

The ions in small cavities provide a greater interaction with the zeolite structure and are in positions that are difficult to access for H_2 molecules. Thus, these cations do not reduce so easily and higher temperatures are required.

It can also be seen that a catalyst that contains only Ni has fewer reducible cations and reduction occurs at temperatures above 700 °C. Although the number of reducible cations is constant throughout the samples, the increase in the intensity of the low-temperature peaks and the decrease for the high-temperature peaks, as Pt is added indicates that Pt helps in the reduction of Ni^{2+}. Similar results have been previously observed for bi-metallic catalysts [11]. A metal that is more easily reduced acts as a site for disassociation of H_2 and nucleation for formation of the second cation [12]. For the bi-metallic Re-Pt-supported on Y zeolite, the same effect was observed—in the presence of Pt the Re cation was reduced at lower temperatures [13].

3.2. Catalytic tests

Fig. 2 shows the activity of catalysts containing 30×10^{-6} atg Me/g cat, with different Ni-Pt ratios, as a function of the reaction time for *n*-hexane isomerization. It can be seen that a catalyst containing only Ni (100Ni0Pt) has negligible activity. However, the addition of 10% Pt (90Ni10Pt) significantly increases the catalyst activity. Fig. 2 also shows that the stability of the 90Ni10Pt catalyst is not very high, going significant deactivation in the first hour of the reaction. The addition of 30 or 40% Pt (70Ni30Pt and 60Ni40Pt) promotes increased activity and the stability

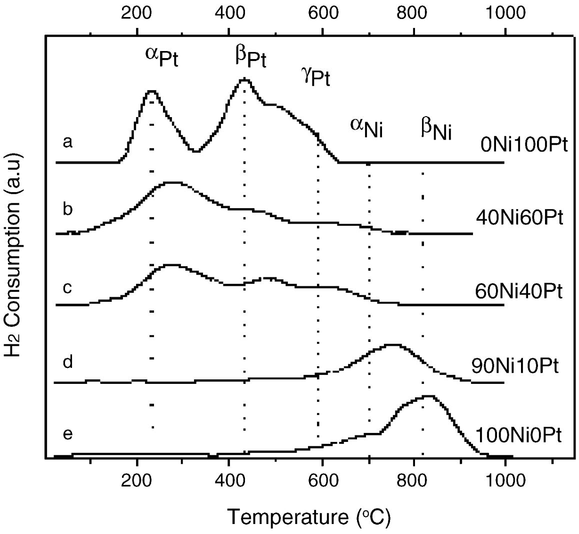

Fig. 1. TPR of catalyst precursors (a–c) with 130×10^{-6} atg of Me/g cat and (d and e) with 180×10^{-6} atg of Me/g cat.

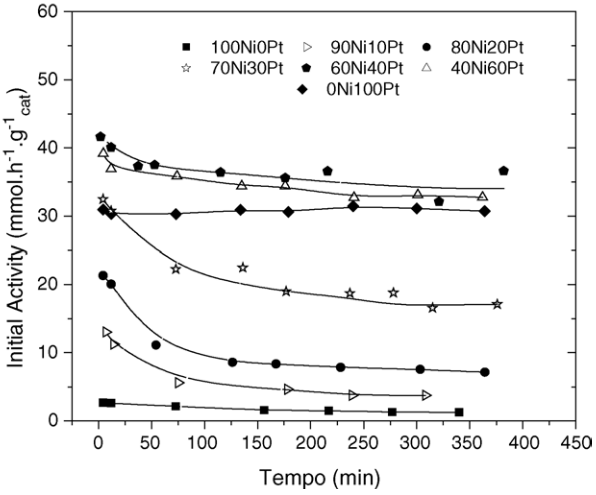

Fig. 2. Activity of monometallic and bi-metallic catalysts with 30×10^{-6} atg Me/g of total catalyst for 6 h reaction time.

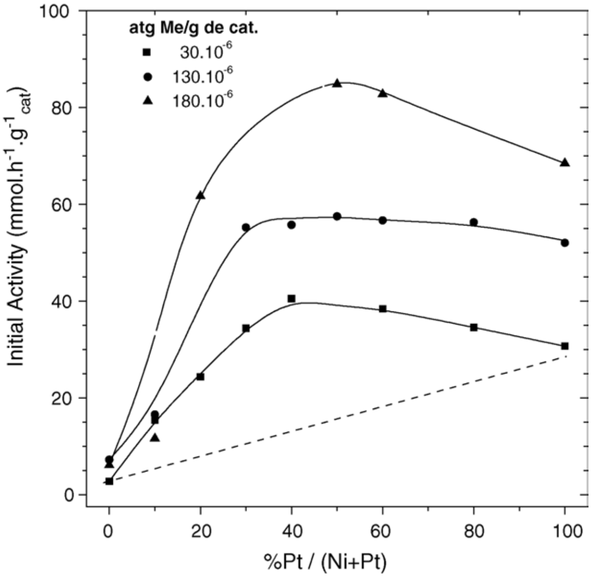

Fig. 3. Initial activity of the Ni-Pt bi-metallic catalysts as a function of the total cation content and % Pt.

of the resulting catalyst. It is curious to see that the replacement of Ni for of 60 or 100% Pt (40Ni60Pt and 0Ni100Pt) results in increased catalyst stability, while the activity for *n*-hexane isomerization decreases. Similar results to those shown in Fig. 2 were achieved for catalysts with higher metal contents—130 and 180 × 10^{-6} atg Me/g cat.

In Fig. 3, results from the initial activity of mono- and bi-metallic Ni-Pt/HUSY catalysts are shown. Results shown in Fig. 3 have been achieved by extrapolating the activity curves (such as those shown in Fig. 2) to $t = 0$. The tests were performed with three initial metal compositions (30 × 10^{-6}, 130 × 10^{-6} and 180 × 10^{-6} atg Me/g cat). Results show that catalysts with higher metal content are more active. To explain this increase, other authors [9,14] have reported that there are a large number of acidic sites available on the HUSY zeolite, so, the metallic sites become the limiting factor to the degree of a catalyst activity. This being true, increased catalyst activity should be expected when the metal content is increased.

Fig. 3 also shows that for catalysts containing low quantities of Pt the activity increases at the same rate as the percent of the metal in the solid. This behavior has been seen for all metal contents (30 × 10^{-6}, 130 × 10^{-6} and 180 × 10^{-6} atg Me/g cat), and it is most certainly due to the greater a Pt activity compared to Ni for *n*-hexane oxidation. However, if catalytic activity were simply the sum of the properties of Ni and Pt, it would then follow the dashed line shown in Fig. 3.

Table 1
H_2 chemisorption

Catalyst	Q_1	Q_2
70Ni30Pt	0.061	0.203
60Ni40Pt	0.311	0.778
40Ni60Pt	0.387	0.645
0Ni100Pt	0.461	0.461

Q_1 = cc/g cat (CNTP); Q_2 = cc/% Pt.

Table 1 shows the quantities of H_2 chemisorbed on catalysts that contain 130 × 10^{-6} atg Me/g cat and it can be seen that, as expected, there is increased Q_1 as Pt content increases. Chemisorption on Ni is low under these conditions, while the relationship between chemisorbed H_2 and % Pt (Q_2) can be seen to pass through a maximum—in a similar manner to the behavior noticed in the activity of the same catalyst. There is, however, another factor that contributes to the catalytic activity and chemisorption of the bi-metallic catalysts, which is probably caused by the degree of Pt dispersion, as reported by other authors [9,14].

Results from a very similar catalyst system achieved with electron microscopy (HRTEM) [14] shows that as Pt content increases, the number of metallic particles also increases, while their average diameter decreases. Furthermore the bi-metallic catalysts have a high concentration of Pt atoms at the outer surface of the particles and, consequently, Ni may be in their core. These results agree with smaller temperature reduction for Ni cations in the presence of Pt, observed in TPR (Fig. 1) and they explain the changes of initial catalytic activity for hexane isomerization with increased Pt content (Fig. 3).

3.3. Catalyst selectivity

Fig. 4 displays the relationship between isomers with one (mono) or two branches (di), as a function of the % Pt. A study on the distribution of these products is significant because bi-ramified isomers have higher octane ratings (RON = 92 or 102) than mono-ramified isomers (RON ~ 74).

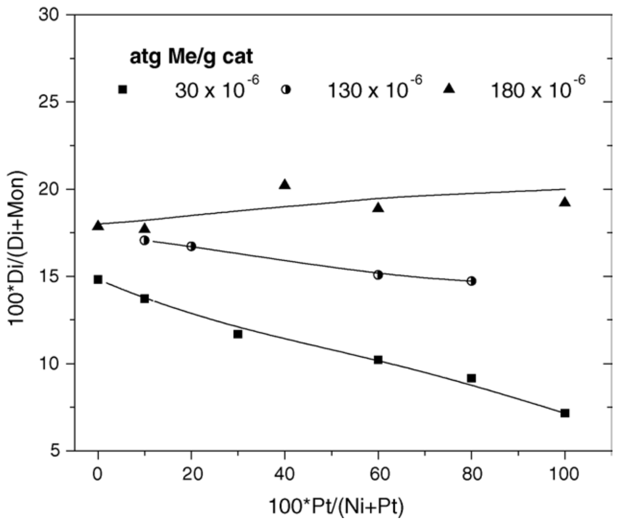

Fig. 4. Selectivity of product formation as a function of total cation content % Pt.

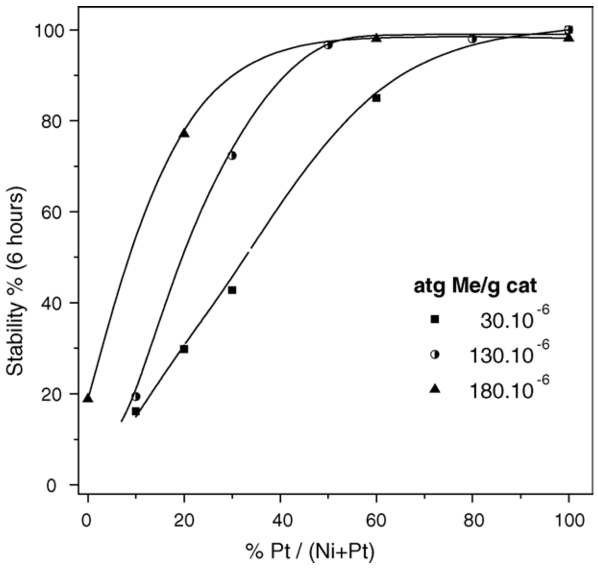

Fig. 5. Catalysts stability as a function of total cation content and Pt %.

As seen in Fig. 4, monometallic catalysts that contain Ni are more selective for the formation of bi-substituted isomers than those containing Pt. It can also be seen that the formation of di-ramified isomers decreases as Pt is added to a Ni catalyst. However, the influence of Pt decreases as the total metal content in the catalyst increases. The selectivity for the formation of di-ramified isomers becomes more emphasized as the total metal content increases from 30 to 130 × 10^{-6} atg Me/g cat, while obtaining catalysts that have higher initial activity (Fig. 4).

For a catalyst with 180 × 10^{-6} atg Me/g cat, the monometallic Pt catalyst is more selective for the formation of di-ramified isomers when compared to that of Ni. The selectivity for these isomers increases at the same rate as % Pt increases.

Fig. 5 shows the catalysts stability, which is defined as the relationship between the final activity (after 6 h) and the initial activity. As can be seen, catalysts containing only Ni tend to lose activity while stability increases as Pt is added to the catalyst. Stability also increases as the total metal content increases, until achieving (in this case) a reasonable level of stability ($E \sim 100\%$) when % Pt is approximately 50%.

3.4. Isomer yield

In Fig. 6, yields of di-ramified isomers are shown for both mono- and bi-metallic catalysts at $t = 0$. These measurements were performed with three different total metal contents (30, 130 and 180 × 10^{-6} atg Me/g cat). The isomer yield is shown as a function of % Pt.

From Fig. 5, it can be seen that the yield of di-ramified isomers depends on the total metal content and on the percent of Pt present, with the yield being higher when both metals are present in similar ratios.

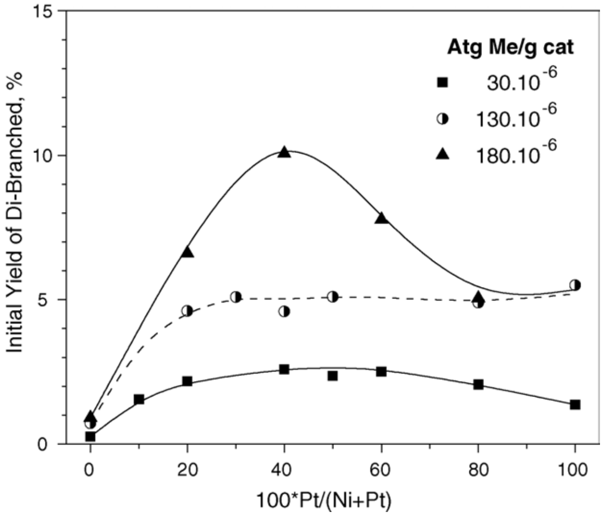

Fig. 6. Yield of di-ramified alkanes as a function of total cation content % Pt ($t_{\text{reaction}} = 0$).

A catalyst with 180 × 10^{-6} atg Me/g cat provides a higher yield due to the larger number of metallic sites available in the HUSY zeolite. With this, acidic sites become the limiting factor for the activity, stability and yield of isomers associated with the catalyst. This being true, it is expected that the yield will increase as the metal content increases.

4. Conclusion

TPR profiles for monometallic catalysts show peaks at temperatures that indicate the probable position of the metal cations in the cavities of the zeolite. TPR results show that Ni-containing catalysts are more easily reduced when in the presence of Pt. This causes a slower reduction to Ni^{2+} reduction temperature. This behavior can be explained by considering the greater Pt facility to disassociate hydrogen, thus facilitating the reaction with the metal cation.

Pt presence in Ni-containing catalysts helps increase the catalytic activity for the isomerization of *n*-hexane, passing through a maximum when the Pt content is 40% or higher. Therefore, working with bi-metallic catalysts is more worthwhile than monometallic catalysts.

Monometallic Ni catalysts are more selective to bi-substituted isomer formation, but the catalytic activity is low. However, when small amounts of Pt are added to the catalysts maximum activity and reasonable product selectivity are obtained. Similar behavior was seen on the stability, thus obtaining stable catalysts when the Pt content is 50%.

A catalyst with 180 × 10^{-6} atg Me/g cat has the highest yield of di-ramified alkanes. This is due to the large quantity of metallic sites available on the zeolite. This makes the number of acidic sites the limiting factor for the activity, stability and yield.

Thus, Ni-Pt bi-metallic catalysts are better than mono-metallic catalysts for the isomerization of *n*-hexane. This is due to the fact that they have higher activity, stability and selectivity.

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